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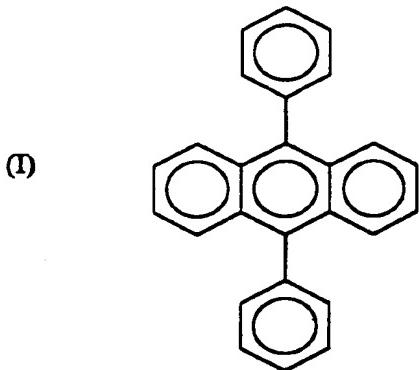
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(54) **Reusable heat-sensitive colour imaging material.**

(57) An imaging material that can repeatedly develop and erase an image, provide high color density and high gradation and is stable when exposed to heat and light, is provided.

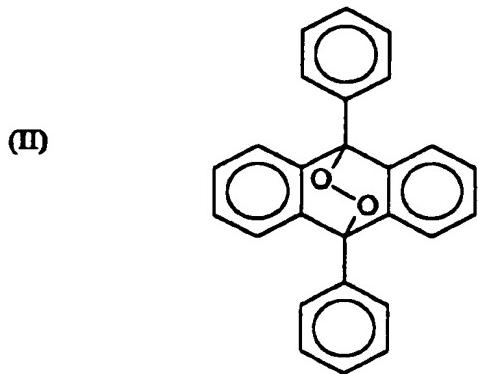
A heat sensitive color material possessing a substrate, a color material layer laminated on the surface of said substrate, and a protective layer on said color material layer, characterized in that said color material layer comprises 100 parts by weight of a binder resin and 20 to 30 parts by weight of an aromatic polycyclic compound containing a 9,10-diphenylanthracene structure represented by the following formula :



or a corresponding endoperoxide construction represented by the following formula :

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DETAILED DESCRIPTION OF THE INVENTION

Field of Utilization in Industry

5 The present invention relates to a erasable and re-recordable recording media for forming letters and images by electric signals, and a recording process using such a recording media. In particular, it relates to a recording media and a recording process that can provide a reversible recorded image usable in printers, facsimiles, and copying apparatus, and is easily maintained and operated.

10 Prior Art

Conventionally, electric photographic processes, thermal transfer processes, ink jet processes, etc. have been suggested and put into practical use as processes for obtaining hard copies. All of these processes, however, relate to the formation of permanent images and, thus, are disadvantageous in that they cannot satisfy the need for erasability and rewritability which is one of the aspects of recent various recording methods.

15 In order to solve the problems, many recording materials utilizing photochromic compounds such as spiropyran, furgides, spiroxazine have been proposed. For example, Japanese Unexamined Patent Publication No. 61-184536 describes a recording material using spiropyran. Such a recording material is erasable and recordable, but is a so-called positive-type recording material, and therefore has limited applications. Moreover 20 such a recording material is very unstable when exposed to heat and light, and is difficult to use in natural light.

Therefore, Japanese Unexamined Patent Publication No. 50-1732 discloses a so-called negative-type recording material showing reverse photochromism, using spiropyran and color-developing by heat.

Such a recording material is negative-type and has wide applications, but provides an unstable image and 25 is substantially difficult to use in natural light. Moreover, it provides low color density, and insufficient gradation.

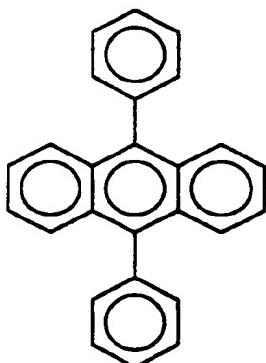
Problem to be Solved by the Invention

This invention is to provide an imaging material that is re-writable, provides high color density and high 30 gradation and is stable when exposed to heat and light.

Means for Solving Problem

In order to solve the above object, this invention provides a heat sensitive color material possessing a substrate, a color material layer laminated on the surface of said substrate, and a protective layer on said color 35 material layer, characterized in that said color material layer comprises 100 parts by weight of a binder resin and 0.1 to 30 parts by weight of an aromatic polycyclic compound containing a 9,10-diphenylanthracene structure represented by the following formula (I):

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55 or a corresponding endoperoxide construction represented by the following formula (II):

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Detailed Description

A transparent or translucent substrate may be used as the above substrate, including various kinds of paper, macromolecular films, plastics, glasses, metals, etc.

Any binder can be used as the above binder resin as long as it has a film forming ability, the resulting film having excellent transparency, and good compatibility with the color material. For example, cellulose, cellulose derivatives, polystyrene, polyester, polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, poly(methyl methacrylate), polyvinyl acetate, etc. can be used. In particular, preference is given to the use of polyester, which has color-developing and -erasing properties.

An available compound such as the above aromatic polycyclic compound includes a compound having a

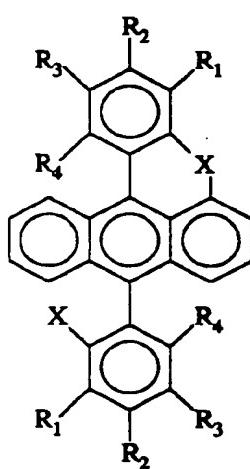
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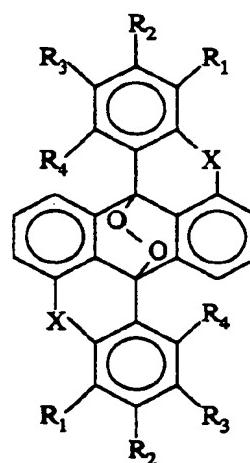
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(III)

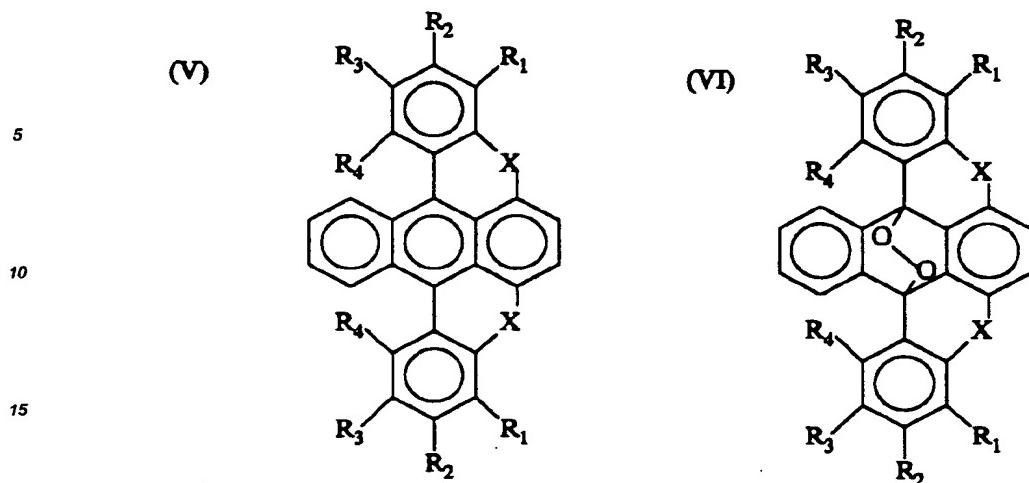


(IV)



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20 wherein X is an oxygen atom, sulfur atom, C=O, or N-R<sub>5</sub>, and R<sub>1</sub>-R<sub>5</sub> are independently, a hydrogen atom, a halogen atom, an alkyl group, a substituted alkyl group, an alkoxy group, a substituted alkoxy group, an aryl group, an aralkyl group, a substituted aryl group, or a substituted aralkyl group, or a corresponding endoperoxide thereof.

25 Preferably, the alkyl groups for R<sub>1</sub>-R<sub>5</sub> are independently a lower alkyl group having 1-5 carbon atoms, such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, tert-butyl group, n-pentyl group, or any other branched pentyl group.

30 Preferably, the alkyl moieties of substituted alkyl groups for R<sub>1</sub>-R<sub>5</sub> are independently a lower alkyl group, for example, and of the alkyl groups mentioned above. The substituents in the substituted alkyl groups are independently, for example, a halogen atom, such as fluorine, chlorine or bromine, or nitro group.

35 Preferably, the alkyl components of the alkoxy groups for R<sub>1</sub>-R<sub>5</sub> are independently a lower alkyl group, for example, any of the alkyl groups mentioned above. Specifically, they are methoxy group, ethoxy group, n-propoxy group, isopropoxy group, n-butoxy group, isobutoxy group, tert-butoxy group, n-pentyloxy group, isopen-tyoxy group, or the like. The alkoxy components of the substituted alkoxy group for R<sub>1</sub>-R<sub>5</sub> are independently, for example, any of the alkoxy groups mentioned above, and the substituents are independently, for example, a halogen atom, such as fluorine, chlorine, or bromine, or nitro group.

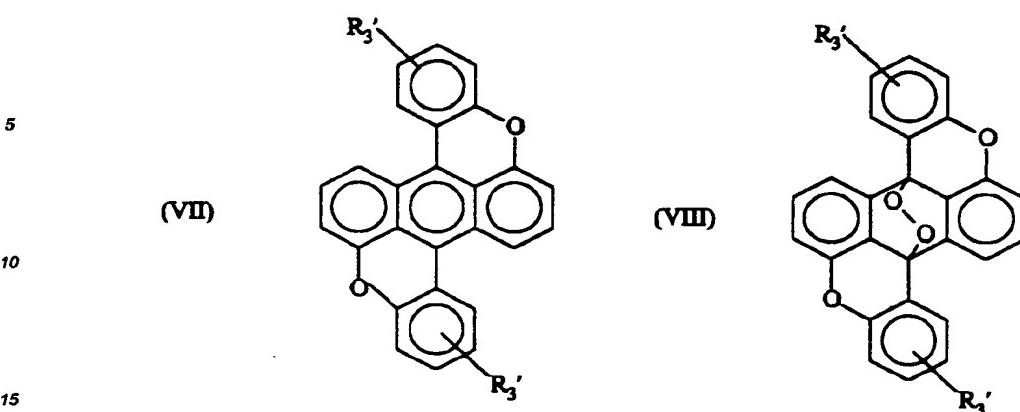
40 The aryl groups for R<sub>1</sub>-R<sub>5</sub> are independently, for example, phenyl group or naphthyl group. The aralkyl groups are independently, for example, a phenyl alkyl group for example a benzyl group. The aryl components and aralkyl components in the substituted aryl groups and the substituted aralkyl groups respectively are, for example, those mentioned above being substituted with a substituent, for example, a halogen atom, such as fluorine, chlorine, or bromine, or nitro group.

A preferable aromatic polycyclic compound according to this invention is benzo[1,2,3-kl : 4,5,6-k'l']dixanetene represented by the following formula (VII) or (VIII):

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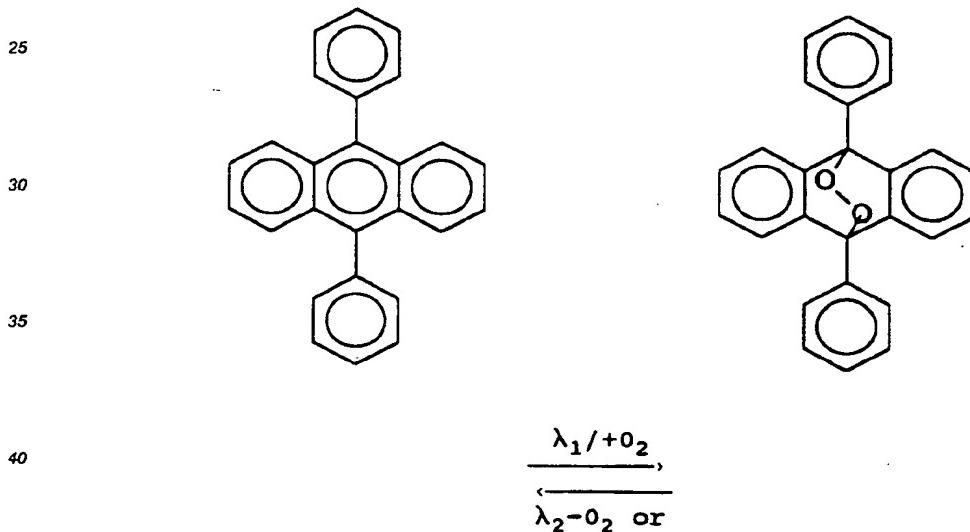
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or its methyl derivative, or a corresponding endoperoxide thereof.

The above-mentioned aromatic polycyclic compound forms a corresponding endoperoxide with the irradiation of a light having a wavelength of  $\lambda_1$  in the presence of oxygen, which further forms the original aromatic polycyclic compound by heating or with the irradiation of a light having a wavelength of  $\lambda_2$ , as represented by the following reaction mechanism:



45 Compounds exhibiting such a reaction are described in H. Durr, H. Bouas-Laurent, editors, "Photochromism" (1990), Chapter 15.

Consequently, the color material according to the present invention can be decolorized with the irradiation of a strong light in the presence of oxygen, and then colored by a heating means, such as a thermal head. The colored material of this invention is very stable in comparison to conventional recording materials using spiropyran, spirooxazine and fulgides, but decolorized with a strong light, for example, of 1 to 1000 J/cm<sup>2</sup>. Accordingly, the color material of the present invention has a high stability in a room light and can be used repeatedly.

As can be understood from the above reaction mechanism, the coloration takes place by entailing the discharge of oxygen on one hand, and the decoloration takes place by entailing the absorption of oxygen. Consequently, to accelerate the decoloration a binder having a high oxygen permeability is preferably used, and to lower the decoloration a binder having a low oxygen permeability is preferably used.

The amount of the above aromatic polycyclic compound or the endoperoxide to be used is in the range of 0.1 to 30 parts by weight, preferably 1 to 20 parts by weight, based on 100 parts by weight of the binder resin. If the amount is too small, the color density is not sufficient, and if it is too large, the dissolution in the binder

is not sufficient, thereby bringing about coagulation.

Any resin can be used as the above protective layer as long as it has heat resistance and slidability to the thermal head, is transparent, and is free of UV curing and heat curing (at 100°C or more). A fluorine resin or silicone resin can be used as such a resin.

5 In the production of the heat sensitive color material according to this invention, it is possible to dissolve the above aromatic polycyclic compound or the endoperoxide and the binder in an appropriate solvent capable of dissolving both components, and to apply the solution on the surface of the substrate, followed by drying. As the solvent in this case, for example, tetrahydrofuran, toluene, chloroform, etc. may be used. The concentration of the binder resin in the solution, which is not specifically restricted, is preferably in the range of 0.1 to 10% by weight, more preferably 1 to 20% by weight.

10 The application of binder resin solution on the surface of the substrate may be carried out in a usual manner, for example, using a Meyer bar, knife coater, gravure coater, die coater, etc. The drying after the application may be carried out, for example, at 50-70°C for 10-60 minutes. Subsequent to drying, the resulting color material layer possesses a thickness of 1 to 50 µm, preferably 3 to 30 µm.

15 With regard to the protective layer, a fluorine resin or silicone resin may be dissolved or uniformly dispersed in a poor solvent that does not affect the color material layer, applied on the surface of the color material layer, and then dried. The poor solvent that can be used in this case includes, for example, an alcohol, hexane or heptane, a furon type solvent, water, or the like.

20 The application of the forming liquid on the surface of the color material layer may be carried out in a usual manner, for example, using a Meyer bar, knife coater, gravure coater, die coater, etc. The drying after the application may be carried out, for example, at 50-70°C for 10-60 minutes. After drying the color material dye layer possesses a thickness of 0.001 to 0.1 µm, preferably 0.01 to 0.1 µm.

25 In the color material having the aromatic polycyclic compound contained in the color material layer according to the present invention, the colored image can be obtained using a totally decolored material and irradiation of visible light by a heating means, such as a thermal head. The colored image can be erased with irradiation of strong visible light.

The colorless material containing a colorless type of aromatic polycyclic compound can form a color image by a heating means, such as a thermal head, and the color image can be decolorized with irradiation of strong visible light.

30 The rate of decoloration depends on the kind of binder used (particularly the oxygen permeability), and the quantum efficiency of the decoloration reaction of the aromatic polycyclic compound. Moreover, when light irradiation for the purpose of the decoloration is carried out, if light irradiation is carried out on the side of the color material layer of the image material the decoloration can take place in a shorter time than when irradiation is carried out on the side of the substrate. The energy required for the decoloration is within the range of 1 to 35 1000 J/cm<sup>2</sup>.

35 The heat sensitive color material according to this invention can be used repeatedly by repeating the image formation by heating and the decoloration of the image with light irradiation.

### Examples

40 This invention will now be described in more detail by referring to the working examples.

#### Example 1

45 72 parts of methyl derivative of benzo[1,2,3-kl : 1,2,3-k'l']dixantene (the compound of formula (VII) where R<sub>3</sub>'=CH<sub>3</sub>) (hereinafter referred to as compound A) and 100 parts by weight of polystyrene (binder resin) were dissolved in 900 parts by weight of tetrahydrofuran (solvent) to prepare a solution. The solution was applied on the surface of a 100 µm thick PET film using a #40 Meyer bar, dried at room temperature for 10 minutes and at 65°C in a dryer for 10 minutes to form a heat sensitive color layer having a thickness of about 10 µm.

50 Thereafter, a solution of 5 parts by weight of Toray silicone (H.V.G.) (produced by Toray Silicone) dissolved in 95 parts by weight heptane was applied as a protective layer with a #40 Meyer bar, and dried at 65°C for 10 minutes to form a red film having a transmission optical density (TOD) of approximately 1.2. This was placed on an OHP (produced by 3M) and decolored over the entire surface with irradiation of light (strength: 100 mw/cm<sup>2</sup>) for 30 minutes to obtain a heat sensitive color material.

55 A sixteen step gradation was formed on the heat sensitive color material thus obtained using a test printer of 3M (200 DPI) by placing a weight of about 4 kg on a thermal head (produced by Kyocera). Thereafter, the entire surface was decolored on the OHP with irradiation of visible light for about 20 minutes, and then a gradation image was formed using the test printer again. The procedure could be carried out repeatedly. The sen-

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sitivity curve at this time is shown in Fig. 1, and the maximum transmission optical density and the transmission optical density at the time of decoloration are shown in Fig. 2.

Examples 2 to 7 and Comparative Examples 1 to 2

5 Various amounts of compound A were dissolved in a 10 wt% solution of polyester resin Vylon 290 (Toyobo) in tetrahydrofuran, applied on 100 micron thick PET films by a #40 Meyer bar, dried at room temperature and placed at 65°C in a dryer for 10 minutes to produce films of Examples 2 to 7 and Comparative Examples 1 to 2. The transmission optical densities of these films were measured using a color transmission densitometer 10 (produced by X-Rite, Model X-Rite 309). The results are shown in Table 1 below.

TABLE 1

Content of Compound based on 100 parts by weight of resin		Transmission optic density	
15	Example 2	0.5	0.15
Example 3	1.0	0.29	
20	Example 4	2.0	0.53
Example 5	3.0	0.72	
25	Example 6	7.2	1.17
Example 7	15.0	1.43	
Comp. Example 1	0.05	0.03	
Comp. Example 2	0.1	0.05	

30 If the amount of compound A where less than 0.5 parts by weight based on 100 parts by weight of the resin, no sufficient transmission optical density could be obtained.

Comparative Example 3

35 A tetrahydrofuran solution of Vylon 290 was added to a given amount of compound A, and tetrahydrofuran was added until compound A was dissolved, then the solvent was removed in a dryer, and the solubility of compound A in the resin was visibly observed. As a result, the coagulant was formed when the amount of compound A exceeded 30 parts by weight.

Example 8

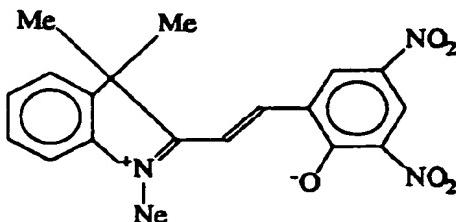
40 7.6 parts by weight of compound A and 100 parts by weight of polystyrene (binder resin) were dissolved in 900 parts by weight of tetrahydrofuran (solvent), the solution was applied on a 100 mm thick PET film, dried at room temperature for 10 minutes, placed at 65°C in a dryer for 20 minutes to obtain a film having a transmission optical density of approximately 1.1.

Comparative Example 4

45 Compound B represented by the following formula:

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10 was prepared by dehydration condensation between 5-dinitrosalicylic aldehyde and 1,3,3-trimethyl-2-methylenindolin.

15 2.5 parts by weight of compound B and polycarbonate (binder resin) were dissolved in 900 parts by weight of 1,2-dichloroethane (solvent), the solution was applied on a glass plate, and spontaneous drying gave a film having a transmission optical density of approximately 1.1.

15 A visible light was irradiated on the films obtained in Example 8 and Comparative Example 4 using a color transmission densitometer (produced by X-Rite, Model X-Rite 309), and the decrease in the transmission optical density was measured. The results are shown in Fig. 3. The colored image from Example 8 was found to be more stable than that from Comparative Example 4.

20 BRIEF DESCRIPTION OF THE INVENTION

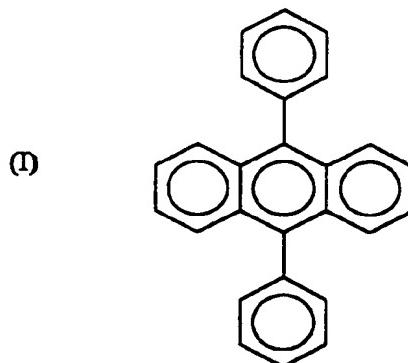
Fig. 1 shows the change in gradation of an image in the heat sensitive color material of Example 1 in the case where the image formation and image decoloration were repeated three times.

25 Fig. 2 shows the changes in image density and density after decoloration (TOD) in the heat sensitive color material of Example 1 when image formation and image decoloration were repeated six times.

Fig. 3 is a graph comparing the stability (color-fading due to irradiation of visible light) of the image of heat sensitive color material prepared in Example 5 with that from Comparative Example 5.

30 Claims

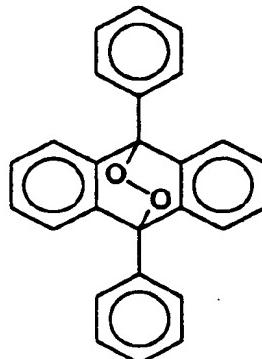
- 35 1. A heat sensitive color material possessing a substrate, a color material layer laminated on the surface of said substrate, and a protective layer on said color material layer, characterized in that said color material layer comprises 100 parts by weight of a binder resin and 0.1 to 30 parts by weight of an aromatic polycyclic compound containing a 9,10-diphenylanthracene structure represented by the following formula (I):



55 or a corresponding endoperoxide construction represented by the following formula (II):

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(II)



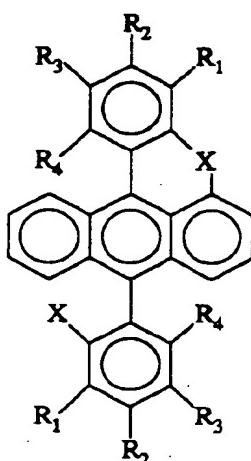
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2. The color material according to claim 1, wherein said aromatic polycyclic compound is a compound represented by the following formula (III), (IV), (V) or (VI):

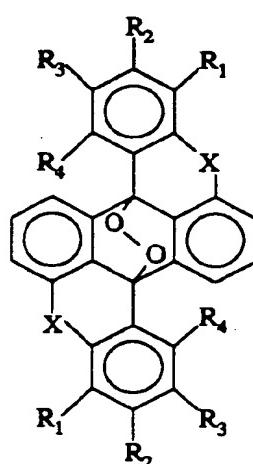
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(III)



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(IV)

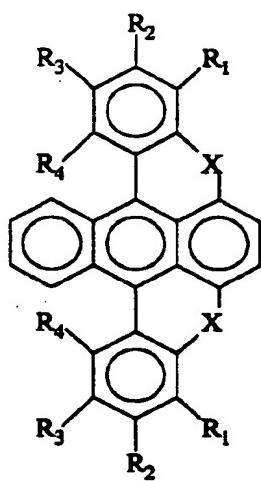


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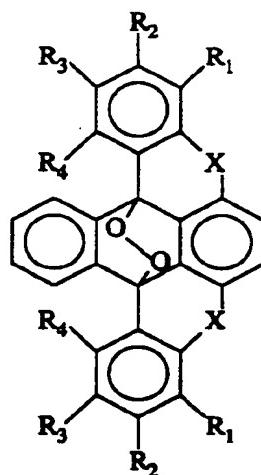
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(V)



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(VI)



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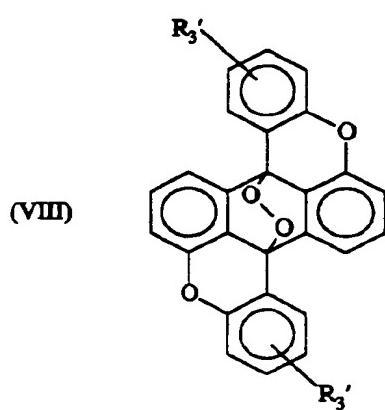
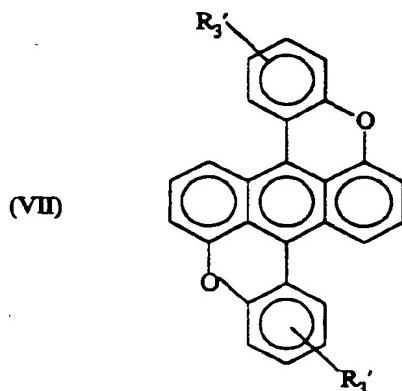
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wherein X is oxygen, sulfur, C=O, or N-R<sub>5</sub>, and R<sub>1</sub>-R<sub>5</sub> are independently, a hydrogen atom, a halogen atom, an alkyl group, a substituted alkyl group, an alkoxy group, a substituted alkoxy group, an aryl group, an aralkyl group, a substituted aryl group or a substituted aralkyl group, or a corresponding endoperoxide thereof.

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3. The color material according to claim 2, wherein said aromatic polycyclic compound is benzo[1,2,3-kl : 4,5,6-K' ,l']dixanetene represented by the following formula (VII) or (VIII):

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or its methyl derivative or a corresponding endoperoxide thereof.

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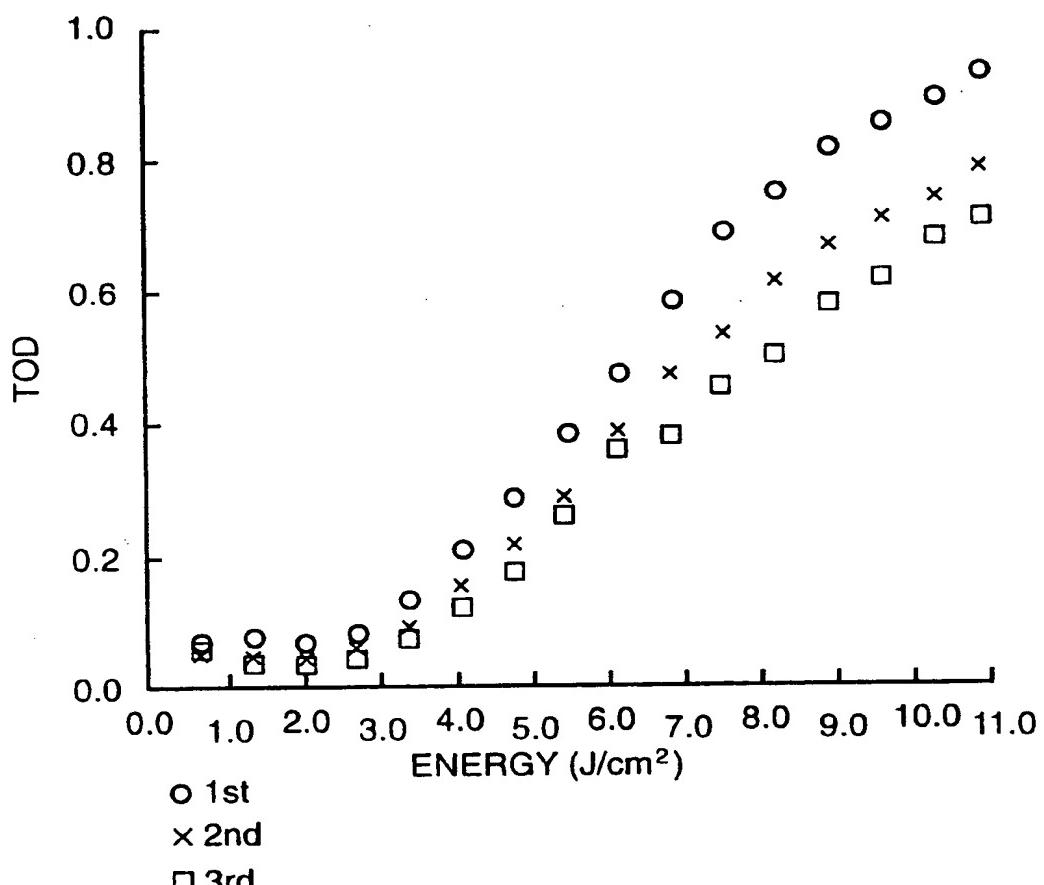
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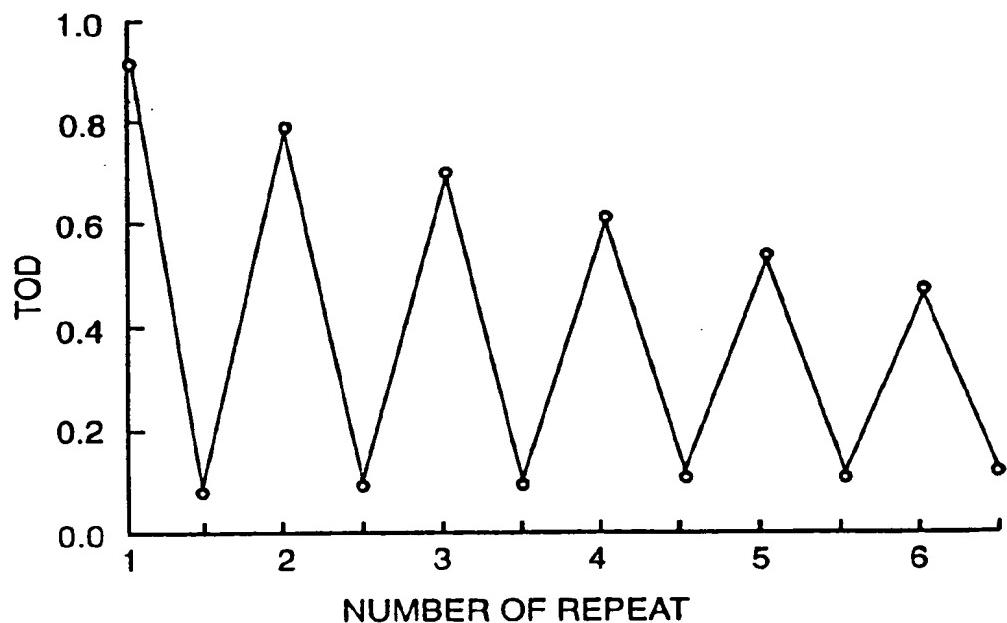
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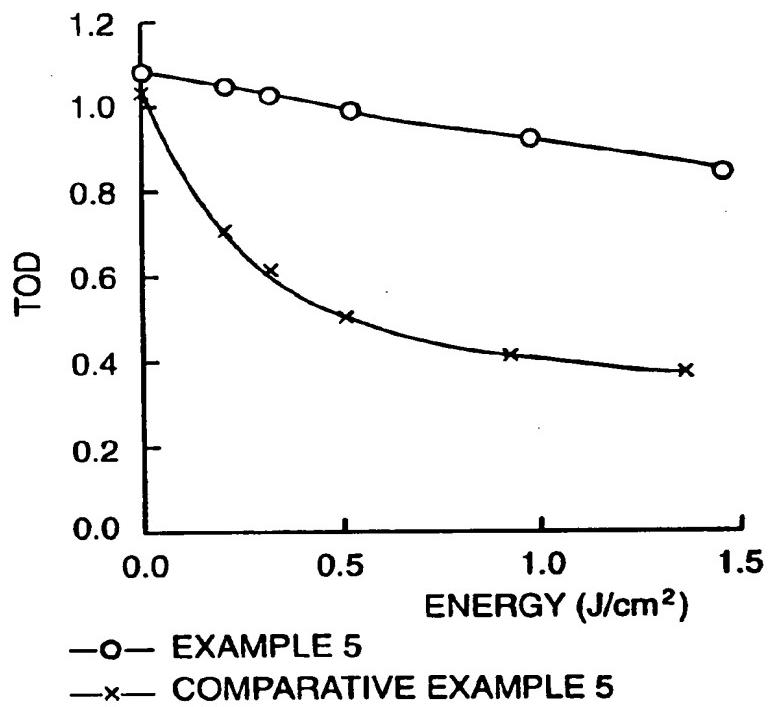
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**FIG. 1**



**FIG. 2**



**FIG. 3**